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CHARACTERIZATION OF PRODUCTS FROM THE CONVERSION OF FURANIC COMPOUNDS TO HYDROCARBONS ON ZEOLITE USING GAS CHROMATOGRAPHY/MASS SPECTROMETRY AND GAS CHROMATOGRAPHY/FOURIER TRANSFORM INFRARED SPECTROMETRY

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ABSTRACT

Products from the conversion of model furanic compounds to hydrocarbons on zeolite ZSM-5 were analyzed using gas chromatography/mass spectrometry (GC/MS) and gas chromatography/Fourier transform infrared (GC/FTIR) spectrometry. The conditions used cover temperatures from 350 to 450°C and space velocities from 0.5 to 2 LHSV. Major individual compounds were positively identified with both techniques while some minor compounds could be partially identified from the complementary information given by both GC/MS and GC/FTIR.

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CARACTÉRISATION DES PRODUITS DE CONVERSION DE COMPOSÉS FURANIQUES EN HYDROCARBURES SUR ZÉOLITHE PAR CHROMATOGRAPHIE EN PHASE GAZEUSE/SPECTROMÉTRIE DE MASSE ET PAR CHROMATOGRAPHIE EN PHASE GAZEUSE/INFRAROUGE À TRANSFORMÉE DE FOURIER

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RÉSUMÉ

Les produits de la conversion de composés modèles dérivés du furane en hydrocarbures sur zéolithe ZSM-5 ont été analysés par chromatographie en phase gazeuse/spectrométrie de masse (GC/MS) et par chromatographie en phase gazeuse/infrarouge à transformée de Fourier (GC/FTIR). Les conditions utilisées pour la conversion couvrent des températures entre 350 à 450°C et des vitesses spatiales entre 0.5 et 2 LHSV. L'identité des composés majeurs a été confirmée par les deux techniques. Certains composés mineurs ont été partiellement identifiés grâce à la complémentarité du GC/MS et du GC/FTIR.

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INTRODUCTION

Research on new sources for liquid fuels is necessary in view of the possible shortage of conventional sources in the future and the difficulties and high costs related to the production of liquid fuels from synthetic crude oils. Biomass is a possible source for the production of liquid fuels especially in the gasoline range as well as for premium octane enhancing additives. Upgrading studies are performed at Laval University using biomass or biomass related model compounds for the production of new liquid fuels. These studies will also help to better understand the reactions occurring on zeolite ZSM-5 and therefore will also be relevant to the production of synthetic crudes from other sources.

This report summarizes the results of the characterization of products obtained from the conversion of model furan-type molecules to hydrocarbons under a variety of conditions. Samples were generated by Dr. S. Kaliaguine's research group at Laval University. After quantification, the samples were submitted to the Energy Research Laboratories for characterization as part of a cooperative program initiated earlier (1). Gas chromatography/mass spectrometry (GC/MS) and gas chromatography/Fourier transform infrared spectrometry (GC/FTIR) were used to identify individual components and to assess the changes in the composition of the products in relation to the experimental conditions.

EXPERIMENTAL

The upgrading experiments were performed at Laval University using a zeolite ZSM-5 in the form of hydrogen. The reactor was filled with 1g of catalyst in a powder form which was not diluted. Experimental conditions include temperatures from 350 to 450°C and space velocities from 0.5 to 2 LHSV. Helium was also fed to the reactor at approximately 6.5 to 7 mL/min. The reactor was operated at atmospheric pressure ($P < 2$ psig). The products were collected as an aqueous solution which was extracted with chloroform. The samples were then sent to the Energy Research Laboratories for analysis. In the meantime, partial exploration of volatile material might have occurred. The purpose of the analysis was to identify the major components produced during upgrading. Quantitation of these components had already been done at Laval University.

The MS system consists of a Balzers QMG 511 quadrupole analyzer combined with an Incos data system. This system is attached to a Varian Vista 6500 gas chromatograph. The outlet of the GC column is positioned directly into the source for maximum transfer of sample to the MS source. The FTIR spectrometer is a Nicolet 60SX equipped with a GC interface by which it is attached to a Varian Vista 6000 gas chromatograph. Both chromatographs are equipped with a 60-m DB-5 capillary column for direct comparison of samples. The initial temperature of 60°C was increased at 4°C/min up to 200°C where it was held for 17 min.

RESULTS AND DISCUSSION

Compound Identification

The identity of the compounds was determined by comparison with standard compounds when they were available. This was the case for molecules having a low level of substitution. When standards were not available for the more substituted samples, GC/MS and GC/FTIR were both used to confirm the identity of the peaks. However, the MS library contains over 30,000 compounds while the FTIR library only contains about 3,000 entries. Therefore, the small size of the FTIR library restricts the number of components that can be confirmed by both techniques. When confirmation was not possible, the GC/MS results were generally sufficiently informative to give a positive identification. For example, the molecular ion indicating the molecular weight and the comparison of retention time with a possible parent compound complement the spectrum in order to identify a peak. One drawback is that MS spectra cannot always identify isomers which can be done with FTIR. Tables 1 to 4 identify the products that were detected in the samples. One can notice that in several cases where the compounds are present as traces, the FTIR was not able to detect them. But when present in large concentrations, the compound identity is confirmed by FTIR when the spectrum is included in the FTIR library.

Furfural

The first series of experiments was performed using furfural as the starting compound. Table 1 lists the components found in the products for each of the conditions. Both GC/MS and GC/FTIR were used for a tentative identification of the components present in each sample. The relative intensity refers to mass spectrometry since the response is considered to be closer to that of a flame ionization detector. However, one must keep in mind that incomplete extraction with chloroform or evaporation of light components might impair the quantitation. One can see that during the blank run only traces of new compounds are formed indicating that there is no thermal decomposition of furfural at 400°C. On zeolite at 350°C and 1 LHSV, only a small amount of methyl furfural and benzofuran are significantly produced. Increasing the temperature to 400°C promotes the production of benzofuran along with a condensation product of furfural. When the temperature was increased to 450°C the amount of furfural was significantly reduced. Benzofuran is still obtained but new compounds appear, such as toluene, xylenes, indanes and indenes. However, the major component has not been identified by either of the two techniques. MS indicates that it would be a derivative of furfural whereas FTIR confirms that it is an aldehyde. Space velocity was also varied while maintaining the temperature at 400°C. Results are shown in Table 1. At 2 LHSV practically no reaction occurred, except for a very small production of methyl furfural and furanyl ethanone. At 1 LHSV, only benzofuran and 2,2-methylene bis furan were significantly produced. Decreasing the space velocity to 0.5 LHSV promoted the formation of benzofuran. The main

component already noticed for 450°C also appeared but in a much smaller concentration. Furfural itself was completely converted to other compounds. Small amounts of hydrocarbons were identified, such as indane, indene and naphthalene. It is interesting to note that only the more severe conditions would cause extensive reaction of furfural.

Furan

Only two sets of conditions were used for furan, i.e. 350°C - 1 LHSV and 400°C - 2 LHSV. From the results obtained with furfural, one can expect that these two sets of conditions will not lead to extensive conversion. As can be seen from Table 2, furan itself is practically absent from the end products and the products obtained are very similar to the identified products of furfural in the same conditions, i.e., mainly benzofuran. From Tables 1 and 2, it seems that benzofuran is a common product of reaction of furan-type compounds, even at less severe conditions. However, experiments with a variety of other furan-type model compounds did not confirm this assumption.

Other Furan Derivatives

Table 3 gives the nature of the compounds that were identified in the products of reaction of various derivatives of furan on zeolite ZSM-5. As opposed to the results with furfural and furan, benzofuran was not significantly present in the products. As can be expected from results in Tables 1 and 2, there was no extensive conversion of the starting compounds, except for dimethyl tetrahydrofuran. Only in this case could we see a high concentration of hydrocarbons such as alkylated benzenes with no evidence of the starting compound.

Tetrahydrofuran

Table 4 shows the results obtained for THF. No products were found for 350°C - 1 LHSV and 400°C - 0.5 LHSV. This was unexpected since dimethyl-THF did give some hydrocarbon products (Table 3) and since low space velocity (0.5 LHSV) seemed to be more adequate (Table 1). This might be caused by a bad extraction of the samples from the initial aqueous solution. However, it is interesting to note in Table 4 that no significant amounts of oxygen compounds were found in the products. From the previous results on furan-type compounds, it seems that tetrahydrofurans are more easily converted than furans. Since furfural produced significant amounts only at severe conditions, this might indicate that they have to be hydrogenated before they can be converted to hydrocarbons.

CONCLUSIONS

The purpose of this work was only to provide an identification of the major components produced during upgrading of model compounds. It is not possible from these results to describe a mechanism for the conversion of cyclic oxygen compounds to hydrocarbons on zeolite ZSM-5 (hydrogen form). It is not possible either to provide an accurate quantitation because of possible evaporation of volatile material. However, results showed that saturated molecules such as tetrahydrofurans are more easily converted than their unsaturated homologs (furans).

This work allowed us to assess the suitability of GC/MS and GC/FTIR for the analysis of biomass synthetic fuels. Both techniques gave equivalent results with the FTIR library being especially useful to confirm the functionality of the compounds and to differentiate isomers of small hydrocarbon molecules. However, the GC/MS system was more sensitive and the small size of the FTIR library was identified as a serious limitation of the GC/FTIR system. Work will be undertaken in order to build a library which would be appropriate for the oil industry.

REFERENCES

1. Jean, G., Coulombe, S. and Sawatzky, H., "Système de coopération", Division report ERP/ERL 84-12(OP), CANMET, Energy, Mines and Resources Canada, April 1984.

Table 1 - Identification of products from the upgrading of furfural

GC/MS	GC/FTIR	Relative intesity	*
- a - 350°C - 1 LHSV			
Furan	not detected	traces	c
Furfural	Furfural	100	b
5-methyl furfural	5-methyl furfural	5	b
Benzofuran	not in FTIR library	9	a
Methyl benzofuran	not detected	traces	c
- b - 400°C - 2 LHSV			
Furan	not detected	traces	c
Composed close to furfural	not detected	traces	
Furfural	Furfural	100	b
1-(2-furanyl) ethanone	not detected	2	c
5-methyl furfural	not detected	5	b
Benzofuran	not detected	traces	a
Indane	not in FTIR Library	2	a
2,2-methylene bis furan	not detected	traces	c
- c -400°C - 1 LHSV			
Furan	not detected	traces	c
Similar to furfural	some aldehyde	5	
Furfural	Furfural	100	b
Xylene	not detected	traces	a
1-(2-furanyl ethanone)	not detected	traces	c
Phenol	not detected	traces	a
Benzofuran	not in FTIR library	30	a
Indene ?	not detected	1	c
Unknown	not detected	3	
2,2-methylene bis furan	not in FTIR library	5	c
Methyl benzofuran	not in FTIR library	2	c
Methyl indene	not detected	traces	c
Naphthalene	not detected	traces	a
Methyl naphthalene	not detected	traces	c
- d - 400°C - 0.5 LHSV			
Similar to furfural	not detected	4	
Furfural	not detected	4	b
Xylene	not detected	2	a
Unknown	dimethyl phenyl acetaldehyde ?	15	
1-phenyl ethanone? C_3-benzene?	not detected	1	
Phenol	some alcohol	1	a
Benzofuran	not in FTIR library	100	a
Indane	not detected	9	a
Indene	not detected	9	c
Methyl benzofuran	?	11	c
Naphthalene	not detected	traces	a

Table 1 - Identification of products from the upgrading of furfural (Cont'd)

- e -450°C - 1 LHSV

GC/MS	GC/FTIR	Relative intesity	*
Furan	not detected	traces	c
Toluene	Toluene	63	a
Similar to furfural	some aldehyde	5	
Furfural	Furfural	66	b
Xylene	not detected	2	a
Xylene	Xylene	18	a
Xylene	?	3	a
Furfural derivative?	Dimethyl acetal acetaldehyde ?	100	
C_3-benzene	not detected	traces	c
Phenol	not detected	traces	a
1-phenyl ethanone	not detected	traces	c
Benzofuran	not in FTIR library	60	a
Unknown	Unknown	6	
Indane	not in FTIR library	4	a
Indene	Indene	9	c
Unknown	not detected	1	
Methyl benzofuran	not detected	traces	c
Methyl indane	not detected	2	c
Naphthalene	Naphthalene	traces	a

- f - blank run on glass beads 400°C - 1 LHSV

Furfural	Furfural	100	b
1-(2-furanyl) ethanone	not detected	1	c
5-methyl furfural	not detected	2	b
C_3-benzene	not detected	1	c

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* Indicates the method of identification: a-pure compounds, b-MS and FTIR libraries, c-MS library only ("b" could also be assigned to a peak already identified by FTIR in another run and confirmed by the retention time and mass spectrum).

Table 2 - Identification of products from the upgrading of furan

GC/MS	GC/FTIR	Relative intesity	*
	- a - 350°C - 1 LHSV		
5-methyl furfural	not detected	12	b
Benzofuran	not in FTIR library	100	a
Unknown	not detected		
	- b - 400°C - 2 LHSV		
Furan	not detected	traces	c
Toluene	Toluene	1	a
Xylene	not detected	1	a
1-(2-furanyl)ethanone	not detected	2	c
C_3-benzene ?	2-cyclohexanone ?	traces	
Benzofuran	not in FTIR library	100	a
Indane ?	not detected	traces	c
Indene ?	not detected	1	c
2,2-methylene bis furan ?	benzofuran derivative ?	2	
3-methyl 2(3H)-benzofuranone ?			
Methyl benzofuran	Unknown	2	c
Methyl indene	Unknown	traces	c

* indicates the method of identification: a-pure compounds, b-MS and FTIR libraries, c-MS library only ("b" could also be assigned to a peak already identified by FTIR in another run and confirmed by the retention time and mass spectrum).

Table 3 - Identification of products from the upgrading of various furan derivatives

-a- 2,5-dimethyltetrahydrofuran 350°C - 1 LHSV

GC/MS	GC/FTIR	Relative intesity	*
Some diolefin, cycloolefin ?	not detected	6	c
Toluene	Toulene	27	a
A branched diolefin	not detected	6	c
Xylene	p-xylene	37	a
Xylene	m-xylene	100	a
Xylene	o-xylene	39	a
C_3-benzene	Unknown	2	c
Propyl benzene	not resolved	7	c
1-ethyl 2-methyl benzene	1-ethyl 3-methyl benzene	81	c
C_3-benzene	Unknown	3	c
1,2,4-trimethyl benzene	1,2,4-trimethyl benzene	47	b
C_4-benzene	not detected	1	c
Indane	not detected	traces	c
1-methyl 3-propyl benzene	m-diethyl benzene	15	
p-diethyl benzene	p-diethyl benzene	15	b
1-methyl 4-isopropyl benzene	1-methyl 4-isopropyl benzene	1	b
2-ethyl 1,4-dimethyl benzene	alkylated benzene	19	c
Unknown	C_4-benzene ?	1	
1,1-dimethyl propyl benzene	Alkylated benzene	3	c
Methyl indane ?	Unknown	2	
C_5-benzene	Alkylated benzene	2	
Napthalene	Naphthalene	traces	a

-b- 2,5-dimethyl furan 350°C - 1 LHSV

2,5-dimethyl furan	2,5-dimethyl furan	100	b
Toluene	Unknown	6	a
Xylene	not detected	traces	a
Xylene	m-xylene	16	a
3-methyl 2-cyclopenten-1-one	3-methyl 2 cyclopenten-1-one	1	b
2,5-hexanedione	2,5-hexanedione	3	b
Ethyl methyl benzene	1-ethyl 3-methyl benzene	2	b
1,2,4-trimethylbenzene	1,2,4-trimethylbenzene	2	b
1-(methylphenyl)-ethanone ?	some acid ?	1	

-c- 2-methyl furan 350°C - 1 LHSV

No compounds were detected except chloroform. The retention time of the feed compound is probably the same as the chloroform (solvent).

Table 3 - Identification of products from the upgrading of various furan derivatives (Cont'd)

-d- 5-methyl furfural 350°C - 1 LHSV

GC/MS	GC/FTIR	Relative intesity	*
Furfural	not detected	6	b
Xylene	Toluene ?	5	a
5-methyl furfural	5-methyl furfural	100	b
3,4,4-trimethyl-2-cyclopenten-1-one		2	c
4-oxo-pentanoic acid, ethyl ester	ester of succinic acid	4	
Unknown	cyclic ketone ?	6	
Dimethyl benzofuran	benzofuran derivative	2	c

-e- 2-methoxy furan 350°C - 1 LHSV

2-methoxyfuran	No significant results were obtained with FTIR	100	c
2-ethyl cyclopentanone		34	c
Unknown		12	
Xylene		16	a
1-penten-3-one ??		8	
Benzofuran		1	a

-f- Furfuryl alcohol 350°C - 1 LHSV

Furfural	not detected	2	b
Furfuryl alcohol	Furfuryl alcohol	100	b
2,2'-methylene bis furan	not detected	3	c

* indicates the method of identification: a-pure compounds, b-MS and FTIR libraries, c-MS library only ("b" could also be assigned to a peak already identified by FTIR in another run and confirmed by the retention time and mass spectrum).

Table 4 - Identification of products from the upgrading of tetrahydrofuran (THF)

GC/MS	GC/FTIR	Relative intesity	*
	-a- 350°C - 1 LHSV		
Toluene	Toluene	47	a
Xylene	not resolved from next peak	12	a
Xylene	Xylene (m- + p-)	100	a
o-xylene	o-xylene	43	a
Propyl benzene	not detected	2	c
1-ethyl 2-methyl benzene	1-ethyl 3-methyl benzene	25	b
1,2,4-trimethyl benzene	1,2,4-trimethyl benzene	35	b
C_4-benzene	C_4-benzene	2	b
Indane	not in FTIR library	3	a
C_4-benzene	C_4-benzene	3	b
C_4-benzene (ethyl dimethyl)	Alkylated benzene	6	c
Tetramethyl benzene	Tetramethyl benzene	3	b
Methyl indane	Unknown	4	c
	-c- 400°C - 1 LHSV		
Benzene	not resolved from solvent peak	traces	a
Toluene	Toluene	62	a
Xylene	not resolved from next peak	21	a
Xylene	m-xylene	100	a
Xylene	o-xylene	33	a
1-ethyl 2-methyl benzene	1-ethyl 3-methyl benzene	24	b
1,2,4-trimethyl benzene	1,2,4-trimethyl benzene	42	b
Indane	not in FTIR library	traces	a
1-methyl 2-propyl benzene	m-diethyl benzene	4	b
o-diethyl benzene	p-diethyl benzene	1	b
1-ethyl 2,3-dimethyl benzene	Unknown	6	c
1,2,3,5-tetramethyl benzene	1,2,4,5-tetramethyl benzene	2	b
4-methyl indane	Unknown	4	c
Naphthalene ?	Unknown	2	a

Table 4 - Identification of products from the upgrading of tetrahydrofuran (THF) (Cont'd)

GC/MS	GC/FTIR	Relative intesity	*
	-d- 400°C - 2 LHSV		
Toluene	Toluene	97	a
Tetrahydro furfuryl alcohol	Tetrahydrofurfuryl alcohol	3	b
Unknown	Unknown	12	
Xylene	not resolved from next peak	17	a
Xylene	m- + p-xylene	100	a
o-xylene	o-xylene	21	a
Ethyl methyl benzene	1-ethyl 3-methyl benzene	25	b
1,2,4-trimethyl benzene	1,2,4-trimethyl benzene	23	b
C_4-benzene	m-diethyl benzene	1	b
C_4-benzenes	C_4-benzenes	traces	b
	-e- 400°C - 0.5 LHSV		
No peaks were detected	No peaks were detected		

* indicates the method of identification: a-pure compounds, b-MS and FTIR libraries, c-MS library only ("b" could also be assigned to a peak already identified by FTIR in another run and confirmed by the retention time and mass spectrum).